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(54) COMPOSITIONS FOR COLOURING THERMOPLASTIC POLYMERS

(71) We, RHONE-POULENC-TEXTILE, a French Body Corporate of 5 Avenue Percier, 75008 Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions for colouring thermoplastic polymers, especially those which can be melt spun, and to thermoplastic polymers coloured with such compositions. It is an improvement in, or modification of, the invention of my Patent No. 1,249,720.

It is known, from French Patent No. 71/25,362, to introduce into molten masses of polyesters (such as polyethylene glycol terephthalate) an azo dyestuff which is soluble in the molten polymer to produce coloured yarns, and to do so without the use of a coating polymer for the dyestuff, the dyestuff being in the form of pellets. However, the azo dyestuffs in question are generally not sufficiently stable in the molten polyester and may therefore degrade if there is the slightest delay during spinning. Furthermore, the process of this French Patent is rather unsuitable for industrial use, because the dispersion of the dyestuff, introduced in the form of pellets, tends to cause unevenness in colour in the completed yarn, caused by agglomerations of dyestuff. Finally, the dyestuff pellets containing 100% of dyestuff form dust which makes them awkward to handle and makes it difficult to use low percentages, introducing a lack of precision into the measurements which results in difficulties in matching colours which it is desired to reproduce.

It is also known from French Patent No. 1,000,992, to introduce vat dyestuffs and anthraquinone dyestuffs directly into molten masses of polyethylene glycol terephthalate. However, this process is not suitable for industrial use because it does not solve the problem of the method of introducing the soluble dyestuff into the mass to be spun.

In British Specification No. 1,249,720 we have described and claimed a composition of viscosity at least 1,000 poises at ambient temperature (i.e. 20°C), for pigmenting shapable thermoplastic polymers, comprising at least one pigment (defined as including any adjuvant insoluble in the shapable polymer) dispersed in a synthetic coating polymer of low molecular weight and of low melting point, wherein the pigment particles have an average diameter of less than one micron, and the coating polymer is a linear aliphatic polyester of melting point at most equal to 150°C, and preferably 50°—100°C, and melt viscosity at most 20 poises at 150°C. derived from at least one linear aliphatic dicarboxylic acid containing 6 to 12 carbon atoms and at least one aliphatic or cycloaliphatic glycol containing 2 to 6 carbon atoms.

It has now been found that shapable thermoplastic polymers can usefully be coloured with dyestuffs which are soluble therein, the dyestuff being added to the polymer in the form of a composition having a viscosity of at least 1,000 poises at 20°C., and comprising at least one dyestuff soluble in the polymer to be shaped and capable of withstanding, for at least 15 minutes without substantial decomposition, a temperature 10% higher than the melting point of the polymer to be shaped, and, as coating polymer for the dyestuff, a linear aliphatic polyester of at least one linear aliphatic dicarboxylic acid containing 6 to 12 carbon atoms per molecule and at least one aliphatic or cycloaliphatic glycol containing 2 to 6 carbon atoms per molecule, the said polyester being heat-resistant under the conditions used for the subsequent processing of the shapable polymer, having a melting point at most equal to 150°C., and a melt viscosity at most equal to 20 poises at 150°C., and being soluble in, or capable of being finely dispersed in, the polymer to be

shaped. The soluble dyestuffs are preferably of the type defined below, which possess good heat resistance.

Soluble dyestuffs possess several advantages over the pigments used in the invention of the aforesaid British specification: they give more glossy and more diverse colourings, their cost price is a half to a quarter of that of the disperse pigments, and the compositions (generally called master mixes) of the present invention make it possible to avoid the vigorous grinding which is absolutely necessary in the case of the master mixes containing pigments according to the invention of the aforesaid specification.

The shapable thermoplastic polymers which may be coloured by the compositions of the present invention include, more particularly, polyesters such as polyethylene glycol terephthalate, polybutylene glycol terephthalate, and their mixtures, polyamides such as those produced from hexamethyleneadipamide, polycaprolactam and their mixtures and polyolefines.

The polymer for coating the dyestuffs is derived from a linear aliphatic dicarboxylic acid containing 6 to 12 carbon atoms per molecule, and a linear aliphatic or cycloaliphatic glycol containing 2 to 6 carbon atoms per molecule. This polyester must be heat-resistant under the conditions used for the subsequent processing of the shapable polymer and have a melting point at most equal to 150°C., preferably between 50 and 100°C. Its melt viscosity is at most 20 poises at 150°C. Examples of suitable polyesters are polyethylene glycol adipate or polyhexanediol adipate, the preferably polyethylene glycol sebacate of molecular weight between 2,000 and 3,000.

The coating polyester is soluble in the polyester to be shaped, such as polyethylene glycol terephthalate, and insoluble in polyamides, but becomes finely dispersed in polyamides such as, e.g. Nylon-6,6, to give very fine particles of the order of a few microns across, which also makes any grinding unnecessary.

The soluble dyestuffs used in the invention must be able to withstand, for at least 15 minutes, a temperature 10% higher than the melting point of the polymer to be shaped.

In the description and the examples which follow, the C.I. references of the dyestuffs mentioned, when they are indicated, relate to Colour Index, 1971 edition. Failing this, the dyestuffs are referred to by their trade mark.

Soluble dyestuffs suitable for colouring polyesters by the present invention include the following: condensation azo dyestuffs such as "Yellow 4610" (of Ciba-Geigy); benzimidazole derivatives such as C.I. Solvent Yellow 106; anthraquinone derivatives such as "Filomon Yellow T 2G" (I.C.I.), "Waxoline Ruby IR" of I.C.I., "Thermoplast Blue RPE" (P.C.U.K.), C.I. Solvent Blue 45 and "Blue H 82455" (I.C.I.); substituted anthraquinones such as C.I. Solvent Green 3 (C.I. 61565); perinone derivatives such as C.I. Solvent Red 135 (P.C.U.K.) and C.I. Solvent Red 162; thioindigo derivatives such as C.I. Pigment Red 181; copper phthalocyanine derivatives such as copper phthalocyanine sulphonamide, e.g. C.I. Solvent Blue 67; some indigo derivatives such as C.I. Vat Red 41 (C.I. 73300); bases of acid dyestuffs such as "Blue RM 1267" (Sandoz) and "Red RM 1264" (Sandoz); xanthene derivatives such as C.I. Solvent Yellow 98 or C.I. Solvent Orange 63, and some mono-azo dyestuffs, although they are at the limit of their thermal stability, such as C.I. Disperse Brown 4 or C.I. Disperse Red 72. Of course, it is also possible to use mixtures of several dyestuffs with one another. Some dyestuffs sold commercially are already mixtures such as Thermoplast Black PLS-PS of Produits Chimiques Ugine-Kuhlman (mixture of an anthraquinone dyestuff and a perinone derivative).

The dyestuffs which are suitable for polyamides include the following: metal azo dyestuffs such as C.I. Solvent Yellow 83, C.I. Solvent Red 92, C.I. Acid Red 313, C.I. Acid Red 359 and C.I. Solvent Yellow 21; and some anthraquinone dyestuffs, such as C.I. Acid Blue 80.

The dyestuff and the coating polymer are first mixed. This operation can be effected with any suitable known mixer, at a temperature which is both above the melting point of the aliphatic polyester and sufficiently high for the molten mass to have a viscosity at most equal to 20 poises. This temperature is not above 150°C. The duration of the mixing depends on the amount of material treated, the temperature of the molten mass and the efficiency of the mixer.

In the examples which follow, an apparatus with a double planetary and scraping stirring action, heated to 130°C. by the flow of heating fluid, was used. In this way, the dyestuffs are dispersed as a homogeneous paste in the aliphatic polyester. The mixture obtained is poured onto a cooling belt and the material is then broken up into particles of the desired size. With an apparatus of this type, for 400 kg of material, the total time for melting and mixing is approximately 3 hours. The homogeneous mixture obtained can be stored very satisfactorily in the solid state. It is not liable to soil and can be easily handled.

The dyestuff is usually mixed with the coating polymer in a proportion of 20 to 60% by weight relative to the weight of

the mixture, and at these concentrations it can easily be finely dispersed.

The dyestuff/coating polymer mixture is mixed directly as granules with the molten mass of the polymer to be shaped, for example in the barrel of a screw extruder. It is possible to introduce the granules of the master mix into the extruder at the same time as the polymer granules using a metering balance, or to introduce the molten master mix measured by a metering pump into the barrel of the extruder. The proportion of the master mix relative to the polymer to be shaped may be, for example, 0.1 to 5% by weight.

In the case where it is desired to produce yarns, the latter, after spinning, may be stretched and optionally further treated in the usual way using any appropriate known method.

The shaped articles obtained possess excellent fastness to light. They also possess very good resistances to wear (4—5 to 5 in the tests for fastness to washing, drycleaning, and steam described below).

The Examples which follow illustrate the invention. In the Examples, the fastness tests are made using the method from the Collection of French Standard Specifications compiled by A,F,N,O,R, The light fastness test using the Xenotest is the subject of ratified French Standard Specification NF G 07,067 (Recommendation ISO R 105/V—1969). The test of fastness to washing at 40°C. is the subject of ratified French Standard Specification NF G 07,015 (Recommendation ISO/R 105/IV—1968). The test of fastness to drycleaning (treatment with perchloroethylene) is the subject of French Standard Specification G 07,070. The test of fastness to steam at 130°C. is the subject of French Standard Specification G 07,044 (Recommendation ISO/R 105/IV—1968). The numbering of the light fastness test ranges from 1 to 8, and that of the other tests from 1 to 5.

The dyestuffs used in the Examples are those which survive the following heat test favourably, 4 g of the dyestuff to be tested (corresponding to 0.2% based on the polymer) and 0.3% of a wetting agent are added to 2,000 g of polymer. The whole is carefully homogenised in a mixer for 10 minutes. A coating of the dyestuff on the polymer is produced by the wetting agent which facilitates its good distribution and attachment to the grains. The mixture is then extruded in an extruder of diameter 40 cm to give a rod which is cooled in a tank through which cold water flows. The rod obtained, of diameter 2 mm, is cut up into small cylinders of length 3 mm to give the powder to be moulded. The pass through the extruder is carried out at 275°C. for polyethylene glycol terephthalate and 285°C. for polyhexamethylene-adipamide. The powder to be moulded is then passed through an injection moulding press to manufacture 3 different small plates under the following conditions:

Polyester:
1st small plate at 275°C. for 3 minutes
2nd „ „ at 285°C. „ 3 „
3rd „ „ at 285°C. „ 15 „

Polyamide:
1st small plate at 285°C. for 3 minutes
2nd „ „ at 290°C. „ 3 „
3rd „ „ at 290°C. „ 15 „

For each type of polymer, the three plates are examined individually and comparatively; in particular, the good dispersion of the dyestuff (evenness of the colour), its solubility in the polymer (transparency), its intensity, and its shade are examined. The dyestuff tested is regarded as suitable for use if the three small plates do not show any difference in shade or intensity between them. Moreover, in order that the polyesters can be shaped in the described manner without undergoing degradation, the latter, containing 1.5% by weight of dyestuff, should have a viscosity index at least equal to 400.

The polyethylene glycol sebacate used in the following Examples has a melt viscosity at 150°C. of 3—6 poises.

EXAMPLE 1

80.933 kg of polyethylene glycol sebacate of melting point 76°C. are melted, while being stirred slowly, in a tank with a double jacket through which a heating fluid at 120°C. flows. 19.067 kg of C.I. Solvent Blue 45 are added in powder form. The mixture is stirred vigorously for one hour. The 100 kg of the homogeneous mixture obtained are poured onto a cooling belt and are broken up into flakes with excellent storage properties.

The master mix thus obtained as flakes is melted in a melting apparatus with a double jacket, heated by steam under pressure at 120°C. The molten mixture is injected into a twin screw extruder supplied with granules of polyethylene glycol terephthalate at the rate of 2% relative to the weight of polymer using a gear metering pump (with a double jacket heated by steam at 100°C.). The injected mixture dissolves completely in the molten polyethylene glycol terephthalate at 285°C. and the mixture obtained at the outlet of the extruder is injected into spinnerets supplying a loom for manufacturing a non-woven web. After calendering and needle-punching the web, a web of filaments based on polyethylene glycol terephthalate is obtained which has

a very uniform and glossy blue colouring, an excellent appearance, and good fastness.

	Fastness
light	6
drycleaning with perchloroethylene at 30°C.	5
washing at 40°C.	5
steam treatment at 130°C.	5

EXAMPLE 2

64.667 kg of polyethylene glycol sebacate of melting point 76°C. are melted, while being stirred slowly, in a tank with a double jacket through which a heating fluid at 120°C. flows. 35.333 kg of C.I. Solvent Green 3 are added as a powder. After stirring vigorously for one hour, the 100 kg of the homogeneous mixture obtained are poured onto a cooling belt and are broken up into flakes with excellent storage properties.

The master mix thus obtained is melted at 120°C. and is injected, by means of a gear metering pump with a double jacket heated to 100°C., into a single-screw extruder supplied with dry granules of polyethylene glycol terephthalate. The proportion of master mix injected is 0.75% based on the polymer to be shaped, and it dissolves completely therein. The coloured molten polymer is injected into a row of spinnerets supplying a loom for manufacturing a non-woven web. After calendering and needle-punching, the web of filaments obtained is coloured intense green, has an excellent appearance, and possesses very good general fastnesses.

	Fastness
light	6
drycleaning with perchloroethylene at 30°C.	5
washing	5
steam treatment	4—5

EXAMPLE 3

50 kg of polyethylene glycol sebacate are melted, while being stirred slowly, in a tank with a double jacket through which a heating fluid at 130°C. flows. The following dyestuffs are added in powder form: 3.846 kg of C.I. Disperse Red 72, 26.923 kg of C.I. Disperse Brown 4, and 19.231 kg of the dyestuff: Thermoplast PLS-PS of Produits chimiques Ugine-Kuhlman. The mixture is malaxated for one hour using a planetary stirrer. The 100 kg of homogeneous mixture obtained are poured onto a cooling belt and are broken up into solid flakes which can be stored indefinitely.

The master mix is melted at 130°C. and is injected using a gear metering pump with a double heating jacket (100°C.), into a twin screw extruder supplied with dry granules of polyethylene glycol terephthalate, in a proportion of 2.60% by weight based on the polymer. The master mix dissolves completely in the polyethylene glycol terephthalate at 285°C., colouring it brown. The polymer thus coloured is spun in the conventional manner, stretched and cut into fibres. The latter have a dark brown colouring with a pleasing glossy appearance, and possess very good fastnesses, which are particularly valuable for woven fabrics intended for clothing. The fastnesses to the various treatments are as follows:

	Fastness
light	7
drycleaning with perchloroethylene at 30°C	5
washing at 40°C.	5
steam treatment at 130°C.	5

EXAMPLE 4

50 kg of polyethylene glycol sebacate are melted, while being stirred slowly, in a tank with a double jacket through which a fluid heated to 120°C. flows. 50 kg of C.I. Disperse Red 72 in powder form are added. The molten mixture is malaxated for one hour with planetary stirring and the 100 kg of the homogeneous mixture obtained are poured onto a cooling belt, and broken up into solid flakes with excellent storage properties.

The mixture is melted and injected, in the same way as in the preceding Examples, at the rate of 4% by weight based on the weight of polyethylene glycol terephthalate into a twin screw extruder. The master mix dissolves completely in the polyester at 285°C., colouring it intense red. The molten polymer is spun and the filaments are then stretched and cut to give fibres of gauge 3.3 dtex/filament. The red fibre obtained has a glossy appearance and excellent general fastnesses, and can be used advantageously in the hosiery trade.

	Fastness
light	7
drycleaning with perchloroethylene at 30°C.	5
washing at 40°C.	5
steam treatment at 130°C.	5

EXAMPLE 5

80 kg of polyethylene glycol sebacate are melted in the same way as in Example 4 and 20 kg of C.I. Solvent Yellow 83 in powder form are added, with vigorous stirring for one hour. The homogeneous mixture is poured onto a cooling belt and broken up into flakes with excellent storage properties. The master mix thus obtained is melted in a melting apparatus identical to that of Example 1 and is injected into a single-screw

extruder supplied with granules of dry polyhexamethylene-adipamide at the rate of 0.50% by weight relative to the polymer. The master mix forms a fine emulsion and the dyestuff dissolves in the polymer at 285°C. without undergoing degradation. The polymer thus coloured is spun easily and the "gold"-coloured filaments obtained have a glossy, intense colouring and possess excellent general fastnesses.

	Fastness
light	7
drycleaning with perchloroethylene at 30°C.	5
washing at 40°C.	5
steam treatment 130°C.	5

EXAMPLE 6

74.700 kg of polyethylene glycol sebacate are melted as in Example 5, 25.3 kg of C.I. Solvent Red 135 are added, and the whole is stirred vigorously for one hour. The homogeneous mixture is then poured onto a cooling belt and stored in the form of flakes. These flakes are dispensed by a metering balance into the feeding funnel of a twin screw extruder at the rate of 0.90% by weight based on the polyhexamethylene-adipamide supplied to the extruder. The master mix forms a fine emulsion in the molten polymer at 285°C. and the dyestuff dissolves completely therein without undergoing degradation. After spinning in the conventional way, a yarn is obtained which has an intense glossy red colour, an excellent appearance, and good general fastnesses. The yarn, cut into fibres, is advantageously used in the manufacture of carpets.

	Fastness
light	7
drycleaning with perchloroethylene at 30°C.	5
washing at 40°C.	5
steam treatment at 130°C.	5

EXAMPLE 7

A master mix containing the following constituents is prepared: 30.000 kg of C.I. Solvent Yellow 83, 3.083 kg of 40% ground manganese stearate (light stabiliser), and 69.917 kg of polyethylene glycol sebacate. The whole is malaxated for 2 hours and the homogeneous mixture is poured onto a cooling belt and the product is thereafter broken up into flakes.

The master mix thus obtained is melted in a melting apparatus heated by a double jacket containing steam at 120°C., taken up in a gear metering pump and injected into a single-screw extruder heated to 285°C. and supplied with granules of polyhexamethylene-adipamide. The master mix becomes finely dispersed in the molten polymer and the dyestuff dissolves completely therein. After spinning and stretching in the usual way, a golden yellow fibre is obtained which has very good light fastness and very good resistance to weathering, and can be employed for open air uses. The fastnesses are as follows:

	Fastness
light	7—8
drycleaning with perchloroethylene at 30°C.	5
washing at 40°C.	5
steam treatment at 130°C.	5

WHAT WE CLAIM IS:—

1. Composition for colouring a shapable thermoplastic polymer having a viscosity of at least 1,000 poises at 20°C., and comprising at least one dyestuff soluble in the polymer to be shaped and capable of withstanding, for at least 15 minutes without substantial decomposition, a temperature 10% higher than the melting point of the polymer to be shaped, and, as coating polymer for the dyestuff, a linear aliphatic polyester of at least one linear aliphatic dicarboxylic acid containing 6 to 12 carbon atoms per molecule and at least one aliphatic or cycloaliphatic glycol containing 2 to 6 carbon atoms per molecule, the said polyester being heat-resistant under the conditions used for the subsequent processing of the shapable polymer, having a melting point at most equal to 150°C., and a melt viscosity at most equal to 20 poises at 150°C., and being soluble in, or capable of being finely dispersed in, the polymer to be shaped.

2. Composition according to claim 1 in which the coating polymer has a melting point between 50 and 100°C.

3. Composition according to claim 1 or 2, in which the coating polymer is polyethylene glycol sebacate.

4. Composition according to claim 3, in which the polyethylene glycol sebacate has a molecular weight of between 2000 and 3000.

5. Composition according to claim 1 substantially as described in any one of the foregoing Examples.

6. A shapable thermoplastic polymer coloured by a composition according to any of claims 1 to 5.

7. A polymer according to claim 6, which is a polyester.

8. A polymer according to claim 7, which is polyethylene glycol terephthalate.

9. A polymer according to claim 6, which is a polyamide.

10. A polymer according to claim 9, which is polyhexamethylene adipamide.

11. Shaped articles produced from a coloured polymer according to any one of claims 6 to 10.

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